Pilot Plant Fixed-Bed Ion-Exchange Resin System for Removing Iodine-131 and Radiostrontium from Milk[1]

H. E. WALTER, A. M. SADLER, D. G. EASTERLY, and L. F. EDMONDSON
Dairy Products Laboratory
Eastern Utilization Research and Development Division, USDA, Washington, D. C.

Abstract

Fixed-bed pilot plant ion-exchange columns were arranged for removing both iodine-131 and radiostrontium from milk by passing the milk first through an anion resin column to remove iodine-131, then acidifying to pH 5.3 and passing it through the cation column. This system was tested for removal of the radionuclides, and for the effect on flavor and composition of whole milk.

More than 93% of iodine-131 was removed by this system from milk in vivo labeled with the isotope, and 90% of environmental levels of strontium-90 removed. Although the resin-treated milks were rated slightly lower than control samples by a trained panel, they were considered acceptable and satisfactory as beverage milk. Composition analysis showed that some of the milk fat was adsorbed by the anion resin near the end of an 8-hr run; loss of solids-not-fat was much less.

Several papers have described in detail various procedures of using ion-exchange resins to remove radiostrontium from milk (1, 3, 5–7, 9). When milk is acidified to a pH of 5.3 before resin treatment, 95% of these isotopes can be removed by passing milk through the resin in fixed-bed columns, with only minor changes in the composition and flavor of the milk. Other cationic radionuclides, cesium-137 and barium-140, can also be removed with slight modifications of the procedures. Edmondson et al. (5) described a manually operated, fixed-bed pilot plant system for removing radiostrontium from milk. Sadler et al. (9) more recently reported results of test runs made with automated pilot plant equipment. More than 90% of environmental levels of strontium-90 was removed, and the flavor of the resin-treated milk compared favorably with control samples when judged for beverage quality.

Techniques have also been developed for removing about 90% of iodine-131 by passing milk through columns containing an anion resin (1, 2, 8). Other effective countermeasures for controlling levels of this isotope include: (1) use of uncontaminated rations for dairy cattle, (2) diverting milk into products that can be stored for 40 days, and (3) procuring milk from an area unaffected by fallout. If it should become necessary to remove radiostrontium from milk, iodine-131 removal by ion-exchange may be the most practical of the above countermeasures.

This paper presents results of studies made by using an integrated pilot plant system to remove both iodine-131 and radiostrontium from milk. The milk was passed through a column containing an anion resin to remove iodine-131, then through a cation exchange column to remove radiostrontium.

Equipment and Methods[2]

Anion system. A glass column, 15.2 cm (id) by 152 cm in length was fitted with glass reducers at both ends, each of which reduced the column diameter from 15.2 to 2.54 cm. A 48-mesh stainless steel screen 15.2 cm in diameter was placed between the reducer and the bottom of the column, to support the anion resin. Seventeen liters of resin (Dowex 2-x8, 20–50 mesh) were put in the column. Depth of the resin bed was approximately 91.4 cm.

Cation system. The equipment used for the removal of radiostrontium was the same as that previously described (9).

Adequate hand-operated valves, fittings, pipes, filters, and pumps controlled the flow of milk, rinse water, and of washing and regenerating solutions through the anion resin column. The strontium removal system (cation resin column) was equipped with automatically controlled pumps and valves to complete a predetermined program of milk processing, rinsing, washing, and regenerating.

The following sequential arrangement of equipment was used in the different phases of milk processing. Refrigerated milk tank → positive pump → preheater → filter → anion column → surge tank → control panel → posi-

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[2] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

tive pump → acidification → pH sensor → filter → cation column → neutralization → pH sensor → surge tank → pasteurization.

Pretreatment and regeneration of anion resin. The anion resin, when purchased, was in the chloride form. Strong base resins of the type used in these studies exhibit some degree of residual amines when stored for a considerable time, or when operated in the hydroxyl cycle. To avoid the probability of off-flavors being imparted to the milk, a pretreatment was employed which consisted of alternate base-acid washes. After filling the columns with fresh resin, three resin bed volumes (rbv) of 3 N NaOH were passed downflow through the resin, followed in sequence by 3 rbv of rinse water, 3 rbv of 3 N HCl, and again with rinse water. This complete cycle was repeated three times. Ten minutes were allowed for each separate solution and rinse water to pass through the column. The resin was then regenerated with a chloride-phosphate-citrate buffer solution having the composition recommended by Murthy et al. (7). Weight of each salt in grams per liter, calculated on anhydrous basis, was

Sodium chloride	7.0
Sodium phosphate	12.0
Sodium citrate	47.7

Twenty rbv (341 liters) of this solution were passed through the column at one-sixth rbv per min. After rinsing with water it was ready for the milk cycle.

Regeneration of the cation resin. The cation resin was regenerated with a mixed salt solution of calcium, potassium, sodium, and magnesium chlorides, the quantities of which were selected to equilibrate the resin with the ratio of cations equal to that in the milk (4). This ensures as slight a change as possible in the composition of the milk when passed through the resin. The regenerant (2,422 liters) was pumped downflow at the rate of 166 liters/min for the initial regeneration. This was followed by rinse water until the effluent was chloride-free. Hot water, 72–80 C, was flushed through the resin until the column effluent was 72 C. This controls bacterial development for 24 hr. The column was rinsed with cold water (10–15 C) immediately before use.

Processing of milk for flavor and composition analysis. Cold raw whole milk was heated to a temperature ranging from 13 to 18 C in a plate preheater, filtered in-line, and passed through the anion resin bed into a surge tank at a flow rate of three-eighths rbv/min. During processing the column pressure gradually increased to approximately 1.4 kg/cm^2, because of the accumulation of a small amount of milk fat on the surface of the resin particles. By gradually increasing the milk temperature from 13 to 18 C during an 8-hr operation, the milk flow was maintained without excessive pressure build-up in the column.

For flavor evaluations, samples were taken from the surge tank during the following three time intervals (zero time equals start of run): Sample 1, 16 to 80 min; Sample 2, 160 to 320 min; and Sample 3, 400–480 min. Since the resin columns (both anion and cation) are filled with water before the milk enters, the first fraction of milk passing through becomes diluted with water. This is the reason for the delay of 16 min before taking the first sample through each column.

From the surge tank the milk was pumped through the cation resin system, using techniques established in previous research and development studies (5, 6, 9). Continuous acidification was accomplished by injecting 0.375 M citric acid into a centrifugal mixing pump. The acidified milk was recirculated to the storage tank until a pH of 5.3 was attained. After adjusting the pH, the milk was filtered in-line, to prevent any particles (sediment or fine curd) from entering the cation column. Flow rate of milk through the cation column was 378.5 liters per hour, or one-sixteenth rbv per min. After resin treatment, the milk was neutralized in-line with 1.5 N KOH to a pH of 6.8. The automatic control equipment, described previously (9), was used to control the acidification, filtration, and neutralization steps during the cation cycle.

Since the capacity of the anion resin for iodine-131 is much greater than that of the cation resin for strontium-90, the milk flow was diverted after a period of time, from cation Column I to cation Column II. For flavor and composition analysis, samples of the neutralized milk were taken during the following time periods after the milk began flowing through the cation columns: Sample 1a from Column I, 16–80 min; 2a from Column II, 16–80 min; 2b from Column II, 80–208 min; and 3a from Column I, 16–80 min (after the milk flow had been diverted back to Column I for a second cycle). The milk fractions from which Samples 1a, 2 (a, b), and 3a were taken were the same portions which comprised Samples 1, 2, and 3 obtained from the surge tank after passing through the anion resin, but before entering the cation columns. The time intervals were selected so that samples of the milk effluent obtained near the start of the run, during an intermediate operating time, and near the

TABLE 1

Flavor scores of milk processed by ion exchange procedure for removal of radionuclides

Control		Milk passed through anion resin cycle only					Milk passed through both resin cycles				
Flavor score after		Sample no.	Anion column no.	Time after start of anion cycle	Flavor score after		Sample no.	Cation column no.	Time after start of anion cycle	Flavor score after	
1 day	7 days				1 day	7 days				1 day	7 days
				(min)					*(min)*		
		1	I	16–80	36.1	36.3	1a	I	16–80	35.7	36.6
		2	I	160–320	36.4	36.5	2a	II	16–80	35.1	36.0
36.8	36.7						2b	II	80–208	35.5	36.1
		3	I	400–480	36.0	36.5	3a	I	16–80	35.9	36.1

end of the run could be compared. Flavor evaluation and analyses for composition (milk fat and total solids) were made on all of the samples and compared to controls. For flavor testing the samples were pasteurized and homogenized. No attempt was made to remove the water (approximately 4% dilution) added during the acidification and neutralization steps.

Flavor scores are given in Table 1. Treatment with the anion resin resulted in a slight decrease in the score; a further slight decrease is noted in the scores of samples passed through both columns. There appears to be a slight improvement in the flavor of the resin-treated samples after refrigeration for seven days. Although the resin-treated milks scored slightly lower using the ADSA scoring system than the control samples, they were considered acceptable and satisfactory as beverage milk.

Results of analysis for milk fat and total solids are given in Table 2. The figures have been corrected for the dilution resulting from the acidification and neutralization steps. The anion resin cycle appeared to have no significant effect on the composition during the first 5 hr of operation (compare Samples 1 and 2 with the control). The composition of Sample 3, however, shows a 7.3% decrease in the milk fat content and 3.5% decrease in TS. By difference, only a 2.0% loss in solids-not-fat (SNF) occurred. These results show that some of the milk fat was absorbed by the anion resin near the end of an 8-hr operation. The absorption of SNF was much less.

A comparison of the composition of Sample 1a with 1, and 3a with 3 shows there was no loss of milk solids in the cation columns. Sample 2a was probably diluted with some of the water in the column; the upward trend noted in Sample 2b, taken during a later time interval from the same column, supports this viewpoint.

Removal of radionuclides. Milk in vivo labeled with iodine-131 was collected for seven milkings, then mixed with 3,181 kg of commercial Grade A raw milk. After 18 hr the milk was assayed for iodine-131 activity with an automatic single-channel gamma spectrometer. The activity was 1,798 counts per min per 15-ml sample. Environmental levels of strontium-90, 24 picocuries per liter, were used to study the removal of radiostrontium by the cation resin. The milk was processed in the same manner as that used for the flavor evaluation studies, except that only one cation column was used. As the milk passed through the anion resin column, 15.0-ml samples were taken at the end of 5, 35, 70, 105, 140, and 175 rbv. Sam-

TABLE 2

Composition of milks processed by ion exchange methods for removing radionuclides

Sample no.	Ion exchange column that milk passed through	Time interval sample was collected	Milk composition	
			Milk fat	Total solids
		(min)	(%)	
Control	....	....	3.43	12.31
1	Anion	16–80	3.40	12.21
2	Anion	160–320	3.39	12.24
3	Anion	400–480	3.18	11.88
1a	Anion + Cation I	16–80	3.40	12.35
2a	Anion +	16–80	3.18	11.75
2b	Cation II	80–208	3.23	12.01
3a	Anion + Cation I (2nd cycle)	16–80	3.18	11.97

TABLE 3

Percentages of iodine-131 and strontium-90 removed from milk by ion exchange resins

Removal of I-131 by anion resin		Removal of I-131 and Sr-90 by passing through both resin cycles		
Bed volumes passed through columns	Per cent removal	Bed volumes passed through columns	Per cent of I-131 removed	Per cent of Sr-90 removed
5	94.31	5	94.7	
35	94.06	5	94.71	90.25
70	94.22			
105	93.96	17	94.17	91.50
140	93.94			
175	93.71	28	93.82	89.46

ples were also taken after 5, 17, and 28 rbv of milk had passed through the cation column. The percentages of iodine-131 removed by treatment with the anion resin are given in Table 3, along with percentages both of iodine-131 and of strontium-90 after passing through both resin cycles.

Regeneration of the anion resin. Previous reports describe in detail procedures for regeneration of the cation resin (4, 6, 9). The affinity of iodine-131 for the anion resin is much greater than that of strontium-90 for the cation resin. This fact makes possible the passage of a much greater volume of milk (per unit volume of resin) through the anion resin before regeneration is necessary, than can be put through a cation resin. Conversely, the stripping of iodine-131 from the anion resin is much more difficult than stripping of radiostrontium from the cation resin.

The following discussion describes procedures used to obtain information on distribution of iodine-131 within the anion resin after the milk cycle, and to determine the effectiveness of 2 N HCl for stripping iodine-131 from the resin.

After 8.5 hr of operation (180 rbv), the anion resin column was rinsed downflow with warm water. A core of the resin was removed by inserting a 2.54-cm pipe through the depth of resin bed. After withdrawing the pipe it was cut into 7.6-cm sections and each section assayed for iodine-131 activity. Figure 1 shows the distribution of activity in the resin column. Even after passing 180 rbv through the anion resin, the lower section of the column was relatively unsaturated with iodine-131 (10,000 cpm per 5.0 ml of resin compared to 250,000 cpm at the top of the column).

To determine the effectiveness of 2 N HCl for stripping iodine-131 from the anion resin, 50 rbv were pumped downflow through the column at one-eighth rbv per minute. Samples of the acid effluent were taken every 2.5 bed volumes (20-min intervals) and assayed as previously described (8).

The activity of the effluent, as a function of volume passed through, is plotted in Figure 2. The data indicate that at least 40 rbv of the acid solution are necessary for stripping iodine from the resin.

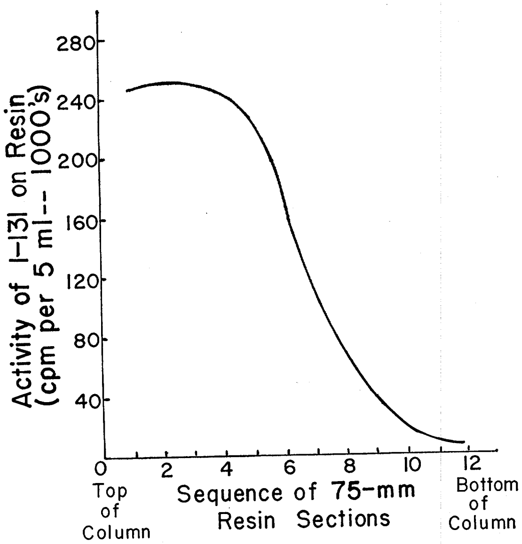

FIG. 1. Distribution of the activity of iodine-131 on fixed-bed anion resin column after milk cycle.

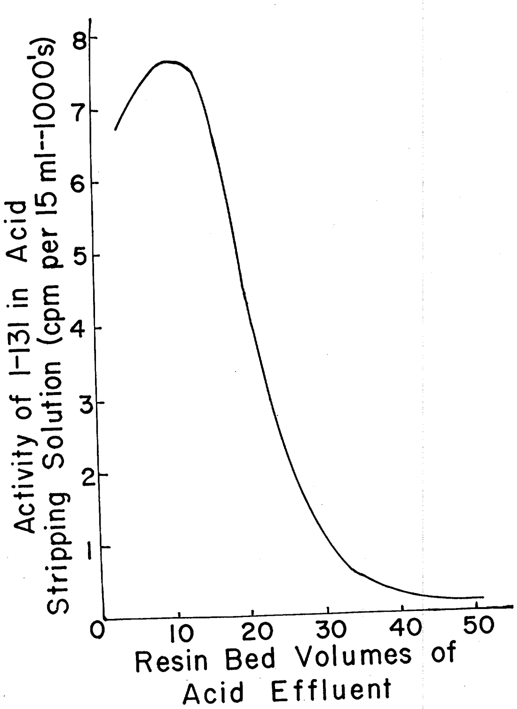

FIG. 2. Activity of iodine-131 in acid effluent after stripping of anion-exchange column with 2 N HCl.

After the acid cycle, the anion column was rinsed and regenerated with the citrate-phosphate-chloride solution in preparation for the next milk cycle.

These pilot plant results show that both iodine-131 and strontium-90 can be removed with an integrated fixed-bed ion-exchange system in which the milk is first passed through the anion resin, then acidified to a pH of 5.3, and passed through the cation resin. The results also show that a product of satisfactory beverage quality can be obtained after the resin treatment.

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